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SOME OBSERVATIONS ON THE FORMATION OF
SURFACE MARTENSITE IN 304L STAINLESS STEEL

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ABSTRACT

A surface martensite was observed in a 304L stainless steel. The morphological details as influenced by polishing techniques and thermal quenching are discussed. The quantity of martensite was found to be greatly amplified by the strain energy produced by mechanical polishing.

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Introduction

A surface-related martensitic transformation has been observed in 18-8 type stainless steels [1,2] and in Fe-Ni alloys [3,4]. In each instance, the transformation was reported to occur spontaneously at temperatures well above the M_s temperatures of the bulk material. This behavior has been interpreted [3,4] as arising from the inability of the surface to support a hydrostatic stress component. This stress is produced by the volume expansion accompanying the $\gamma \rightarrow \alpha'$ transformation. Kaufman et al [4] observed a decrease in the M_s temperature in an Fe-30% Ni alloy of about 5×10^{-3} K-atm⁻¹. The absence of a hydrostatic stress therefore raises the M_s temperature. Klosterman [3] describes the surface martensite formation at 5-30°C above that of the M_s temperature for an Fe-30% Ni alloy.

Just [In this investigation, two distinct morphologies of surface martensite were observed in an annealed 304L stainless steel. No temperature or strain excursions had occurred to prompt the transformation. The study was conducted to examine the morphology and quantity of martensite produced as influenced by the polishing technique.]

Experimental

[The chemical analysis of the alloy was 0.026 percent C, 18.52 percent Cr, 8.75 percent Ni, 1.05 percent Mn and the balance Fe. Although the chemistry is within the allowable range for a 304L alloy, it is atypically low in the elements which are known austenite stabilizers. As a consequence, this alloy has an abnormally high propensity to form martensite. To provide

a measure of the instability of the austenite, the T_0 value was computed. T_0 is defined as the temperature above which martensite cannot thermodynamically form (i.e., $\Delta G^{Y-\alpha'}$ is positive). This analysis has been described in the literature [5]. The alloy used in this study had a T_0 value of 321°C, 50°C higher than for a typical chemistry of 304L stainless steel.

The material had been forged at approximately 900°C followed by a full anneal to conform to a 206 MN/m² yield strength requirement.

Results and Discussion

The microstructure of the as-received material after mechanically polishing and etching is shown in Figure 1. This is contrasted to the microstructure after exposure to -17°C for 45 minutes in Figure 2. Two distinct morphologies of martensite coexist with the austenite matrix: a platelet shaped (spearhead) martensite (position a) which favors nucleation and growth along annealing twin boundaries, consistent with the surface martensite in Fe-Ni-Cr reported by Breedis [6] and a massive-type martensite (position b) which exists intragranularly. Figures 3 and 4 show more clearly the result of the low temperature excursion on the two types of martensite. The existing platelets exhibited growth in both width and length as well as additional nucleation. The massive type exhibited no significant change. Additional exposures to -55°C created no further change in the phase quantities. The magnetic phase content as determined both before and after the low temperature exposures by a Severn indicator¹ and magnetometer

¹Trademark of Severn Engineering Company, Inc., Annapolis, MD.

was less than 0.5% present, although the quantity of martensite indicated by a linear analysis on Figure 2 was approximately 15%. The sample, in the condition indicated in Figure 2, was then inspected by X-ray diffraction to determine the martensite structure. A monochromator was used to eliminate fluorescent radiation. α' -martensite was detected, with one additional weak peak indicating a small quantity of ϵ -martensite.

To discern the martensite phase distribution, the specimen was electropolished to remove 50-75 μm of the existing surface and then etched (Figures 6, 7). The microstructure both before and after the electropolishing procedure is shown in contrast in Figures 5 and 6. As noted, the platelets are almost nonexistent and the massive type has been significantly reduced. An X-ray diffraction scan was unable to detect any martensite. Exposures to -55°C (Figure 8) produced no detectable change in the distribution or quantity of martensite in this electropolished sample.

Conclusions

1. The abnormally low austenite stabilized chemistry prompted the martensite transformation.
2. The martensite is concentrated at the surface and exists in two morphologies: (1) a plate-like morphology described as surface martensite which prefers annealing twin boundaries for nucleation and growth and (2) a "massive-type" morphology which nucleates intragranularly and is not significantly affected by thermal quenching. The diffraction experiments indicate that the structure of the martensite was predominantly the BCC type (α' -martensite).

3. The observed quantity of martensite was greatly influenced by the strain energy imposed during mechanical polishing thus producing an erroneously high quantity compared to the bulk. Level

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Figure 1.
As-received, mechanical polish



Figure 2.
Exposed, -17°C for 45 minutes

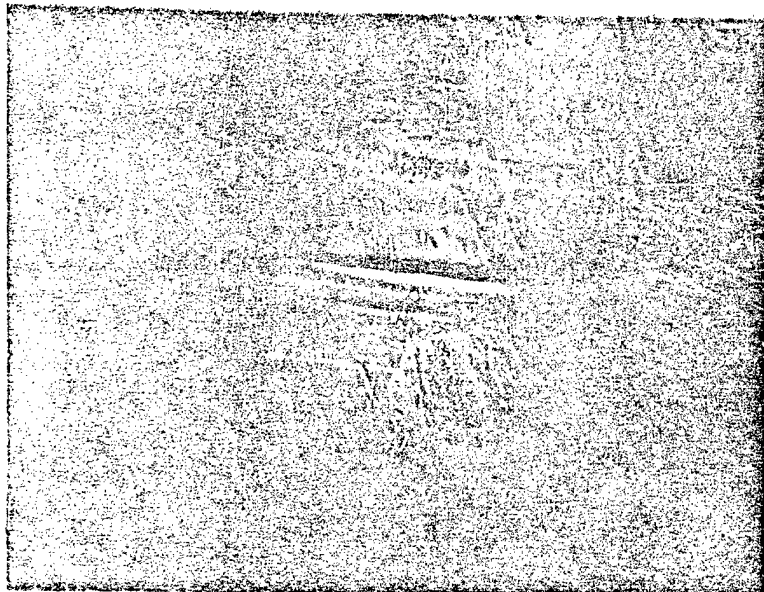


Figure 3.
As-received, mechanical polish

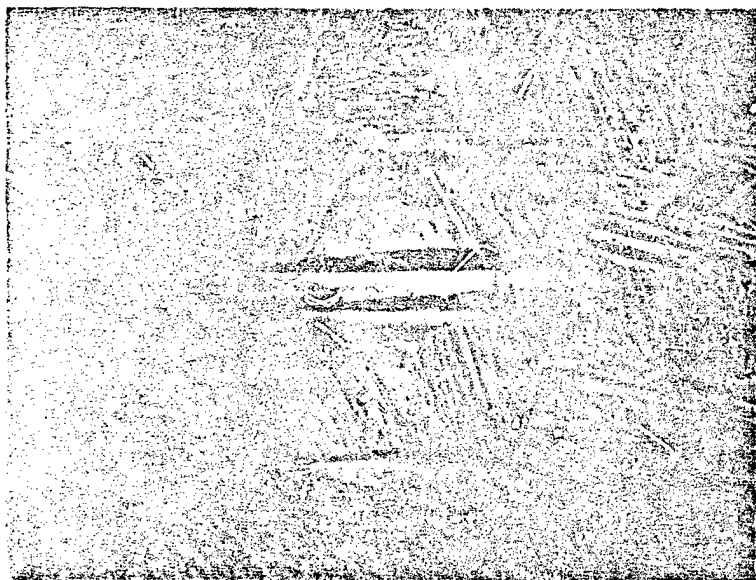


Figure 4.
Exposed, -17°C for 45 minutes



Figure 5.

**Mechanical polish, exposed
to -17°C for 45 minutes**



Figure 6.

**Electropolished to remove
50-75 microns**

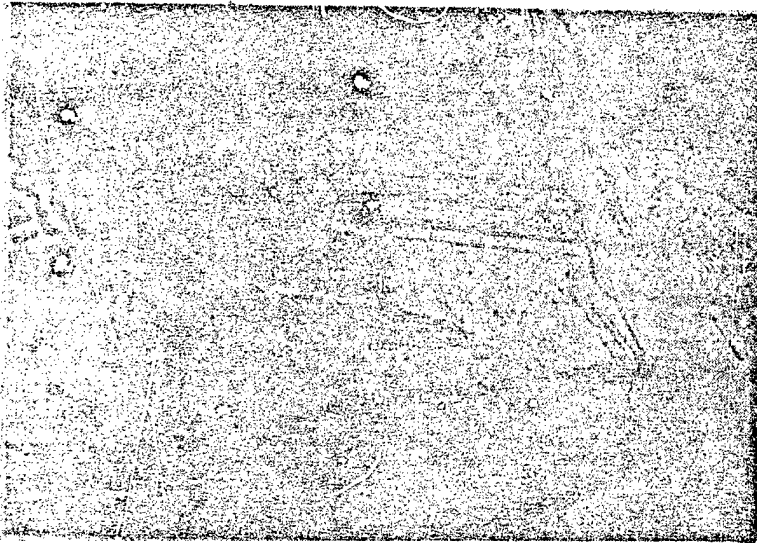


Figure 7.
Electropolished surface
prior to any exposure

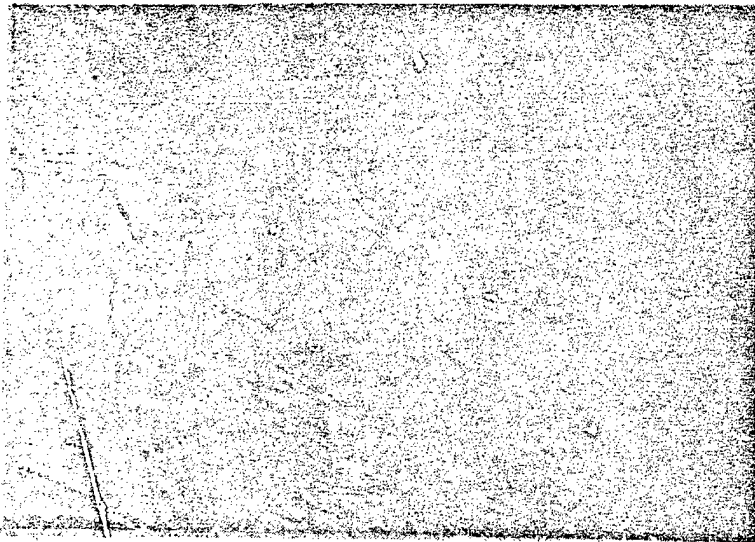


Figure 8.
Exposed, -55°C for 30 minutes:

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